

Exploring the Limits of Gradient Corrections in Density Functional Theory

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Received 2 June 1998; accepted 28 July 1998

ABSTRACT: We have recently proposed a simple and systematic approach to the generation of exchange-correlation functionals in density-functional theory by linear least-squares fitting to accurate thermochemical reference data. In a series of four publications, new functionals with gradient corrections of first and also second order have been found in this way. In the present article we review and summarize our approach, highlighting the common threads and the most extensive fits from the heretofore published studies. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 63–69, 1999

Introduction

In several recent publications,^{1–4} we have attempted to systematize the generation of new exchange-correlation functionals in Kohn–Sham density-functional theory (DFT) by fitting to experimental reference data in what we believe to be a logical and controlled manner. Our methodology encompasses functionals depending on density gradients of first order,^{1,2} commonly referred to as GGAs (generalized gradient approximations), and also a new class of beyond-GGA functionals of second order.^{3,4} In this work, we review the work

of refs. 1–4 with an emphasis on their commonalities, and a focus on the most important fits.

The second and third sections describe the basic analytical structure underlying all the functionals in refs. 1–4. The ideas of these sections are quite general and can be applied to DFT variables of any kind, not just the first- and second-order gradient variables discussed here. In the fourth section, the most extensive and relevant fits from refs. 1–4 are reviewed. Our calibration set is essentially the Gaussian-2 (G2) thermochemical reference data^{5–7} of Curtiss, Raghavachari, and Pople, containing heats of formation, ionization potentials, electron affinities, and proton affinities. We then conclude, in the final section, with cautionary remarks on the applicability of the functionals presented here, and a preview of work in progress to address these issues.

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Exchange-Correlation Functionals: General Form

We assume throughout this work that the exchange-correlation energy has the following general form (where σ is a spin index):

$$E_{XC} = \sum_{\sigma} E_{X\sigma} + E_{C\alpha\beta} + \sum_{\sigma} E_{C\sigma\sigma} \quad (1)$$

namely, a sum of terms for exchange, opposite-spin dynamical correlation, and parallel-spin dynamical correlation respectively. Let us point out that, in molecular bonds, part of what we *loosely* call “exchange” in *local DFT approximations* actually mimics nondynamical, near-degeneracy correlation. We shall not dwell on this point here, but refer the reader elsewhere for elaboration.^{8–10}

In this work, the terms in eq. (1) are given the respective forms:

$$E_{X\sigma} = \int e_{X\sigma}^{\text{UEG}}(\rho_{\sigma}) g_{X\sigma} d^3\mathbf{r} \quad (2)$$

$$E_{C\alpha\beta} = \int e_{C\alpha\beta}^{\text{UEG}}(\rho_{\alpha}, \rho_{\beta}) g_{C\alpha\beta} d^3\mathbf{r} \quad (3)$$

$$E_{C\sigma\sigma} = \int e_{C\sigma\sigma}^{\text{UEG}}(\rho_{\sigma}) f_{\sigma}^{\text{SCC}} g_{C\sigma\sigma} d^3\mathbf{r} \quad (4)$$

where, in each of these integrands, e^{UEG} is the corresponding *uniform electron gas* energy density per unit volume, multiplied by a gradient correction factor g . We shall synonymously refer to the g functions as *inhomogeneity* correction factors. In addition, eq. (4) for parallel-spin correlation contains a “self-correlation” correction, f_{σ}^{SCC} , which assures that the correlation energy of any one-electron system is exactly zero. For the uniform electron gas:

$$e_{X\sigma}^{\text{UEG}}(\rho_{\sigma}) = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3} \rho_{\sigma}^{4/3} \quad (5)$$

For dynamical correlation, we extract $e_{C\alpha\beta}^{\text{UEG}}$ and $e_{C\sigma\sigma}^{\text{UEG}}$ from the *total* UEG correlation energy density, $e_{\text{C}}^{\text{UEG}}$, using the application of Stoll et al.¹¹:

$$e_{C\alpha\beta}^{\text{UEG}}(\rho_{\alpha}, \rho_{\beta}) = e_{\text{C}}^{\text{UEG}}(\rho_{\alpha}, \rho_{\beta}) - e_{\text{C}}^{\text{UEG}}(\rho_{\alpha}, 0) - e_{\text{C}}^{\text{UEG}}(\rho_{\beta}, 0) \quad (6)$$

$$e_{C\sigma\sigma}^{\text{UEG}}(\rho_{\sigma}) = e_{\text{C}}^{\text{UEG}}(\rho_{\sigma}, 0) \quad (7)$$

where we use, for $e_{\text{C}}^{\text{UEG}}$, the parameterization of Perdew and Wang.¹² Also, let us point out that the

well-known “local spin density approximation” (LSDA) corresponds to all the correction factors g (and f_{σ}^{SCC}) equal to unity.

Each of the inhomogeneity corrections g is *assumed* to depend on a *single* dimensionless parameter reflecting local deviation from homogeneity (i.e., uniform electron gas behavior). This is admittedly an approximation, but a very expedient one, because one-dimensional fits to reference data are obviously preferable to higher dimensional fits. Our philosophy, then, is to fully explore the limits of the factorized functional forms of eqs. (2), (3), and (4) before generalizing to more complicated possibilities.

In refs. 1–4, two inhomogeneity measures were considered: the dimensionless or “reduced” (spin) density gradient:

$$s_{\sigma} = |\nabla\rho_{\sigma}|/\rho_{\sigma}^{4/3} \quad (8)$$

commonly used in gradient-corrected density functionals (GGAs) today, and a new inhomogeneity parameter of second order³:

$$q_{\sigma} = (Q_{\sigma} - Q_{\sigma}^{\text{UEG}})/|Q_{\sigma}^{\text{UEG}}| \quad (9)$$

where:

$$Q_{\sigma} = \frac{1}{6} \left[\nabla^2 \rho_{\sigma} - 2\tau_{\sigma} + \frac{1}{2} (\nabla\rho_{\sigma})^2 / \rho_{\sigma} \right] \quad (10)$$

$$\tau_{\sigma} = \sum_i |\nabla\psi_{i\sigma}|^2 \quad (11)$$

and Q_{σ}^{UEG} is given by:

$$Q_{\sigma}^{\text{UEG}} = -\frac{1}{5} (6\pi^2)^{2/3} \rho_{\sigma}^{5/3} \quad (12)$$

Parameter q_{σ} is logically and physically motivated by examination of the two-electron exchange “hole” density at short interelectronic separation, a full development of which is presented in ref. 3. The derivation will not be repeated here to avoid confusion.

Explicitly, then, we consider g functions of the form $g(s_{\sigma}^2)$ or the more sophisticated $g(q_{\sigma})$. To avoid excessive verbosity in what follows, functionals of the s variable will be referred to as “GGA1” (because they involve first-order density gradients only) and functionals of the q variable will be referred to as “GGA2” (because they involve up to second-order density gradients).

Notice that the opposite-spin $g_{C\alpha\beta}$ depends on *both* spin densities and hence on both s_{α}^2 and s_{β}^2 (and other possible crossterms as well) in the case of GGA1, or both q_{α} and q_{β} in the case of GGA2.

Once again, however, to enjoy the expediency of fitting in one dimension only, we make an approximation: that $g_{C\alpha\beta}$ depends on the *average* value of s_α^2 and s_β^2 or the *average* value of q_α and q_β . In detail, therefore, we have, in GGA1, the three gradient-correction factors:

$$g_{X\sigma}(s_\sigma^2), g_{C\alpha\beta}(s_{\text{avg}}^2), g_{C\sigma\sigma}(s_\sigma^2) \quad (13)$$

where:

$$s_{\text{avg}}^2 = \frac{1}{2}(s_\alpha^2 + s_\beta^2) \quad (14)$$

and, in GGA2, we have:

$$g_{X\sigma}(q_\sigma), g_{C\alpha\beta}(q_{\text{avg}}), g_{C\sigma\sigma}(q_\sigma) \quad (15)$$

where:

$$q_{\text{avg}} = \frac{1}{2}(q_\alpha + q_\beta) \quad (16)$$

The parallel-spin correlation energy, eq. (4), contains an additional self-correlation correction, f_σ^{SCC} . As discussed in ref. 3, the function:

$$f_\sigma^{\text{SCC}} = \left[\tau_\sigma - \frac{1}{4}(\nabla\rho_\sigma)^2/\rho_\sigma \right] / \tau_\sigma \quad (17)$$

has the interesting property that it vanishes identically in any one-electron system, and is otherwise always positive and less than unity. Also, f_σ^{SCC} takes unit value in the UEG limit. Therefore, zero correlation energy is guaranteed in the one-electron special case. Note, however, that f_σ^{SCC} is a second-order gradient correction (i.e., through its τ_σ dependence) and is not available in the strictly first-order GGA1 framework. More specifically, then, we have

$$\text{for GGA1: } f_\sigma^{\text{SCC}} = 1 \quad (18)$$

$$\text{for GGA2: } f_\sigma^{\text{SCC}} = \left[\tau_\sigma - \frac{1}{4}(\nabla\rho_\sigma)^2/\rho_\sigma \right] / \tau_\sigma \quad (19)$$

Linearization

Our basic objective is to fit the inhomogeneity correction factors to experimental reference data. For this purpose, the g functions must be conveniently and yet flexibly parameterized.

In the case of GGA1, the gradient variable s^2 has semi-infinite domain:

$$0 \leq s^2 \leq \infty \quad (20)$$

A finite domain is much more convenient for fitting purposes, however, and we therefore intro-

duce the following transformation to a new finite variable u :

$$u = \gamma s^2 / (1 + \gamma s^2) \quad (21)$$

$$0 \leq u \leq 1 \quad (22)$$

We allow a different transformation (i.e., a different value of γ) for each exchange-correlation component, so that we now have three g functions $g_{X\sigma}(u_{X\sigma})$, $g_{C\alpha\beta}(u_{C\alpha\beta})$, and $g_{C\sigma\sigma}(u_{C\sigma\sigma})$ with:

$$u_{X\sigma} = \gamma_{X\sigma} s_\sigma^2 / (1 + \gamma_{X\sigma} s_\sigma^2) \quad (23)$$

$$u_{C\alpha\beta} = \gamma_{C\alpha\beta} s_{\text{avg}}^2 / (1 + \gamma_{C\alpha\beta} s_{\text{avg}}^2) \quad (24)$$

$$u_{C\sigma\sigma} = \gamma_{C\sigma\sigma} s_\sigma^2 / (1 + \gamma_{C\sigma\sigma} s_\sigma^2) \quad (25)$$

The parameters $\gamma_{X\sigma}$, $\gamma_{C\alpha\beta}$, and $\gamma_{C\sigma\sigma}$ are determined by fitting to *atomic* exchange-correlation energies as outlined in the Appendix. We use:

$$\gamma_{X\sigma} = 0.004, \quad \gamma_{C\alpha\beta} = 0.006, \quad \gamma_{C\sigma\sigma} = 0.2 \quad (26)$$

Similarly, the inhomogeneity variable q in GGA2 has infinite domain:

$$-\infty \leq q \leq +\infty \quad (27)$$

which we map to a finite domain through the new variable

$$w = \lambda q / (1 + \lambda^2 q^2)^{1/2} \quad (28)$$

$$-1 \leq w \leq +1 \quad (29)$$

The functions $g_{X\sigma}$, $g_{C\alpha\beta}$, $g_{C\sigma\sigma}$ have respective arguments:

$$w_{X\sigma} = \lambda_{X\sigma} q_\sigma / (1 + \lambda_{X\sigma}^2 q_\sigma^2)^{1/2} \quad (30)$$

$$w_{C\alpha\beta} = \lambda_{C\alpha\beta} q_{\text{avg}} / (1 + \lambda_{C\alpha\beta}^2 q_{\text{avg}}^2)^{1/2} \quad (31)$$

$$w_{C\sigma\sigma} = \lambda_{C\sigma\sigma} q_\sigma / (1 + \lambda_{C\sigma\sigma}^2 q_\sigma^2)^{1/2} \quad (32)$$

with λ values given by (see Appendix):

$$\lambda_{X\sigma} = 0.11, \quad \lambda_{C\alpha\beta} = 0.14, \quad \lambda_{C\sigma\sigma} = 1.6 \quad (33)$$

Both for GGA1 and for GGA2, the g functions are now conveniently defined on a finite domain. An obvious and flexible representation is a *power series expansion*:

$$g = \sum_{i=0}^m c_i u^i \quad (34)$$

with a similar expression in terms of the variable w for GGA2. All the g functions are now specified by linear expansion coefficients up to some finite

(as yet undetermined) order m , and *linear least squares fitting* is therefore an attractive and viable option to determine them. We choose to fit to accurate thermochemical data, as discussed in the following section, but one more detail needs to be addressed.

It has been argued^{8–10} that local exchange-correlation functionals (including the GGA1- and GGA2-types discussed here) fail to capture an essential nonlocality in molecular bonds. Replacement of a small fraction of the approximate DFT exchange with *exactly computed* exchange is the remedy. Exact-exchange mixing is accommodated by adding to eq. (1) an exact-exchange term as follows:

$$E_{XC} = \sum_{\sigma} E_{X\sigma} + E_{C\alpha\beta} + \sum_{\sigma} E_{C\sigma\sigma} + c_X^{\text{exact}} E_X^{\text{exact}} \quad (35)$$

None of the above GGA1 or GGA2 formulas is altered by this, but the first term in eq. (35) no longer represents *all* the exchange energy. The addition of the c_X^{exact} parameter significantly improves fits to thermochemical data in our experience.^{1,3}

Fits to Thermochemical Data

Let us now review the most extensive of our fits from refs. 1–4. Basically, the Gaussian-2 (G2) thermochemical data set of Pople and coworkers^{5–7} is our reference data of choice. These data were compiled for the purpose of assessing the multistep *ab initio* “G2” thermochemical procedure after which the data set is named.

The largest calibration set so far employed in our work consists of:

- 148 standard heats of formation from the extended G2 data set of ref. 7;
- 42 ionization potentials from the original G2 data set,⁵ slightly augmented as in ref. 6;
- 25 electron affinities from the original G2 data set⁵;
- 8 proton affinities from the original G2 data set,⁵ slightly augmented as in ref. 6; and
- 10 *total atomic* energies for H through Ne, from ref. 13

for a total of 233 calibration data altogether. To remain as close as possible to the G2 set itself, we use the same MP2/6-31G(d) geometries and scaled Hartree–Fock zero-point energies and finite tem-

perature corrections¹⁴ as used in the G2 publications. We shall restrict ourselves, in the present study, to this 233-point fit set.

Our electronic structure calculations are fully numerical and *post-LSDA*. LSDA orbitals and densities are computed with the basis-set-free NUMOL program,¹⁵ using the UEG correlation parameterizations of Perdew and Wang,¹² and then substituted into the exchange-correlation terms of the previous sections. This post-LSDA approach allows straightforward linear least-squares fitting to the calibration data, but is admittedly not self-consistent. It is nevertheless a well defined *procedure*, as is G2 theory⁵ itself, which will be further examined in the next section.

For a given expansion order m in eq. (34), the total number of fit parameters, including the exact-exchange coefficient c_X^{exact} in eq. (35), is:

$$p = 3(m + 1) + 1 = 3m + 4 \quad (36)$$

The optimum expansion order m is not known at the outset, however, and needs to be determined essentially by trial. One might naively guess that better functionals can be generated systematically by increasing the order m indefinitely, but this is not the case. GGA1 and GGA2 are *model* functionals only, restricted to first and second-order density gradients respectively. The exact exchange-correlation functional depends, in principle, on *all* gradient orders. Overparameterization of the present models is therefore a danger if (to borrow a graphic analogy) we try too forcefully to fit a “square peg into a round hole.” It is our experience that overparameterized functionals give extremely poor results when applied outside the calibration set.

How, then, do we determine the optimum order m ? In Table I, the “goodness-of-fit” index for a

TABLE I. Goodness-of-Fit (kcal/mol), Eq. (37).

m	GGA1	GGA2
0	9.6	7.2
1	3.2	3.2
2	2.9	2.6
3	2.9	2.6
4	2.9	2.5
5	2.8	2.5
6	2.8	2.5

p -parameter fit to n data points:

$$\text{GoF} = \sqrt{\Delta/(n-p)}, \quad \Delta = \sum_{i=1}^n (x_{\text{model},i} - x_{\text{expt},i})^2 \quad (37)$$

is listed for each of GGA1 and GGA2 for expansion orders $m = 0$ to $m = 6$. The GoF index is essentially the root-mean-square (rms) error per number of *independent* data points. Table I reveals two things. First, GGA2 is superior to GGA1, although perhaps only slightly so. We attribute this to the somewhat more satisfying physical interpretation of the q parameter in GGA2 over the s parameter in GGA1 (see ref. 3). Second, it is clear in both cases that the GoF “levels off” after $m = 2$, suggesting that additional parameters beyond $m = 2$ may not be justified. Inspection of actual plots of the g functions (see ref. 4) confirms this conclusion, in that the plots beyond $m = 2$ display unphysically erratic behavior, particularly at the endpoints. Therefore, we take $m = 2$ as the optimum expansion order in the rest of this work, giving $p = 10$ fit parameters altogether. The actual rms error for each of our 10-parameter, 233-point fits is 2.82 kcal/mol for GGA1 and 2.59 kcal/mol for GGA2.

In Table II, we present mean absolute (and maximum absolute) deviations from experiment for the various subsets of data in the 233-point fit. The heat of formation results are especially encouraging. Mean absolute error is 1.89 kcal/mol for GGA1 and 1.69 kcal/mol for GGA2. Maximum errors are 9.1 and 8.7 kcal/mol, respectively. These error statistics compare fairly well with G2 theory itself (mean error 1.58 and maximum error 8.2 kcal/mol). Proton affinities are also comparable in quality to those of G2 theory, although the sample space (8 data) is too small to draw definitive conclusions. Our ionization potentials and electron affinities, however, show roughly twice the error of G2.

TABLE II. Deviations from Experiment: Average Absolute (Maximum Absolute).

	GGA1	GGA2	G2 ^a
Heats of formation (kcal/mol)	1.89 (9.11)	1.69 (8.65)	1.58 (8.2)
Ionization potentials (eV)	0.12 (0.66)	0.11 (0.65)	0.055 (0.19)
Electron affinities (eV)	0.09 (0.34)	0.10 (0.30)	0.056 (0.15)
Proton affinities (kcal/mol)	1.1 (4.3)	1.7 (2.6)	1.04 (2.0)
Total atomic energies (mH)	4 (7)	3 (8)	

^a G2 values from refs. 5 and 7.

Notice, also, that *total* energies of the atoms H through Ne are accurately reproduced as well, with mean and maximum errors of only 4 and 7 mH for GGA1 and 3 and 8 mH for GGA2. It is very satisfying that our 10-parameter fits deliver not only accurate energy differences, but the total energies themselves. Fitting to total energies only makes sense, of course, in the basis-set limit. Within the context of the presently used post-LSDA procedure, this is where we are with the NUMOL program.¹⁶

Finally, in Table III, the best-fit expansion coefficients in eq. (34) are listed for both GGA1 and GGA2. It is of interest to note how closely the uniform electron gas limit is or is not satisfied by our fits. Because we have not imposed the UEG limit *a priori*, this is an excellent test of physical sensibility. The UEG limit is given by the sum ($c_X^{\text{exact}} + c_{X\sigma,0}$) for exchange, and by $c_{C\alpha\beta,0}$ and $c_{C\sigma\sigma,0}$ for the two components of dynamical correlation. Both GGA1 and GGA2 recover the UEG limit fairly well for both exchange and opposite-spin correlation, which is reassuring. Parallel-spin correlation, on the other hand, is strongly attenu-

TABLE III. Expansion Coefficients, Eq. (34).

	GGA1	GGA2
$c_{X\sigma,0}$	0.790194	0.773335
$c_{X\sigma,1}$	0.400271	0.632816
$c_{X\sigma,2}$	0.832857	0.162037
$c_{C\alpha\beta,0}$	0.934715	1.21707
$c_{C\alpha\beta,1}$	1.14105	-2.25501
$c_{C\alpha\beta,2}$	-5.33398	0.642815
$c_{C\sigma\sigma,0}$	-0.120163	0.063745
$c_{C\sigma\sigma,1}$	2.82332	-0.881634
$c_{C\sigma\sigma,2}$	-2.59412	1.37248
c_X^{exact}	0.219847	0.233095

ated in GGA1 and in GGA2. This may be rationalized, in part, by the arguments of Stoll et al.,¹¹ who pointed out that much of the parallel-spin correlation energy in the electron gas is responsible for cancelling long-range oscillations in the *exchange* hole. Because these exchange-hole oscillations are absent in finite systems, the UEG parallel-spin correlation energy density is a severe overestimate in atoms and molecules. Plots of the best-fit g functions may be found in ref. 2 (GGA1) and in ref. 4 (GGA2).

Conclusions and Outlook

The major conclusion of this work is that exchange-correlation functionals with gradient corrections up to second order can be generated easily and logically by linear least-squares fitting to thermochemical calibration data such as the G2 data set. Our second-order functional is slightly superior to our first-order functional, and both encouragingly approach G2 theory itself in accuracy. These functionals are admittedly 10-parameter fits, but, *regardless of how they are determined*, they are useful and more precise than older functionals such as B3P⁹ or the related B3LYP.¹⁷ The studies of ref. 7, for example, show an average B3LYP heat of formation error of 3.11 kcal/mol, compared with the present 1.89 for GGA1 and 1.69 for GGA2. A possible next step in the refinement of these 10-parameter DFTs is to include weaker interactions in the fit set (e.g., hydrogen bond and van der Waals interactions). Preliminary extrapolation tests (unpublished) are quite positive in this regard.

Some words of caution are in order, however, regarding the general applicability of the present fits. When fitting highly parameterized functionals to calibration data, the results (i.e., the coefficients in Table III) are very sensitive to procedural details and basis sets. The functionals of Table III, therefore, are for *post-LSDA* computations *at the basis-set limit*. If applied to other than LSDA densities and/or with a small or modest basis set, results of the present quality *will not* be obtained. Basis-set incompleteness introduces an artifactual underbinding trend that will certainly degrade the accuracy of these basis-set-limit functionals. The underbinding trend of incomplete bases might be compensated, however, by *refitting* our 10 parameters for each and every basis set of interest. We are currently investigating this pragmatic path

even though it somewhat compromises theoretical rigor.

The technology exists to implement these functionals in a self-consistent manner, even for the second-order GGA2 (see ref. 18 for implementation of a related second-order functional). This work may therefore serve as a useful starting point for self-consistent reparameterizations in standard basis sets.

In the meantime, the present work should be viewed as an exploration of what is ultimately possible with gradient-corrected DFT in the factorized form of eqs. (2), (3), and (4). The consequent one-dimensional fits are very encouraging indeed, and the basic analytical ideas (i.e., transformation of DFT variables to *finite* variables, followed by power series expansion of the functionals) appear to be very generally useful.

Appendix

The fitting of nonlinear parameters to the full calibration set is cumbersome and undesirable. The three GGA1 γ parameters of eqs. (23) to (25) and the three GGA2 λ parameters of eqs. (30) to (32) are therefore predetermined by fitting to *atomic* exchange and correlation energies. This preliminary fit assumes naively simple inhomogeneity corrections, g , to obtain reasonable γ and λ estimates. *Reasonable* estimates are sufficient, because the subsequent least-squares fitting on the full calibration set compensates for any sloppiness.

Exchange energy is underestimated by the LSDA, and the exchange correction, $g_{X\sigma}$, must therefore *enhance* the UEG approximation. The simplest conceivable enhancement factors are:

$$\text{GGA1: } g_{X\sigma} = 1 + u_{X\sigma} \quad (\text{A1})$$

$$\text{GGA2: } g_{X\sigma} = 1 + w_{X\sigma} \quad (\text{A2})$$

These seemingly crude approximations deliver rather good atomic exchange energies if the values of $\gamma_{X\sigma}$ in eq. (23) and $\lambda_{X\sigma}$ in eq. (30) are appropriately chosen. Even though Eq. (A2) unphysically reduces the exchange-energy density to zero at the nucleus (where $w = -1$), the $4\pi r^2$ volume factor renders this artifact unimportant. We find that the values of $\gamma_{X\sigma} = 0.004$ for GGA1 and $\lambda_{X\sigma} = 0.11$ for GGA2 best fit the exchange energies of the noble-gas atoms He through Xe, and these values are used throughout.

A similar procedure is applied to opposite and parallel-spin dynamical correlations. Now, however, the g functions need to *attenuate* the UEG approximation, because the LSDA overestimates correlation energies of atoms. For opposite spins, the simplest conceivable attenuation functions are:

$$\text{GGA1: } g_{C\alpha\beta} = 1 - u_{C\alpha\beta} \quad (\text{A3})$$

$$\text{GGA2: } g_{C\alpha\beta} = 1 - w_{C\alpha\beta} \quad (\text{A4})$$

and for parallel spins:

$$\text{GGA1: } g_{C\sigma\sigma} = 1 - u_{C\sigma\sigma} \quad (\text{A5})$$

$$\text{GGA2: } g_{C\sigma\sigma} = 1 - w_{C\sigma\sigma} \quad (\text{A6})$$

Again, γ and λ values have been appropriately chosen to give good *atomic* energies. Specifically, the exact correlation energies of He and Ne are delivered by $\gamma_{C\alpha\beta} = 0.006$ and $\gamma_{C\sigma\sigma} = 0.2$ in GGA1, and by $\lambda_{C\alpha\beta} = 0.14$ and $\lambda_{C\sigma\sigma} = 1.6$ in GGA2. These values have been adopted throughout this work.

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